# TRANSMITTAL FORM

(to be used for all correspondence after initial filing)

| | |
|---|---|
| Application Number | 09/981,643 |
| Filing Date | October 16, 2001 |
| First Named Inventor | Leo W.M. Lau, et al. |
| Art Unit | 1775 |
| Examiner Name | Archene A. Turner |
| Attorney Docket Number | CUH-003.00/16678US01 |

| Total Number of Pages in This Submission | 23 |
|---|---|

## ENCLOSURES (check all that apply)

☒ Fee Transmittal Form
  ☐ Fee Attached
☒ Amendment/Reply
  ☐ After Final
  ☐ Affidavits/declaration(s)
☐ Extension of Time Request
☐ Express Abandonment Request
☐ Information Disclosure Statement
☐ Certified Copy of Priority Document(s)
☐ Reply to Missing Parts/ Incomplete Application
  ☐ Reply to Missing Parts under 37 CFR 1.52 or 1.53

☐ Drawing(s)
☐ Licensing-related Papers
☒ Petition
☐ Petition to Convert to a Provisional Application
☒ Power of Attorney, Revocation Change of Correspondence Address
☐ Terminal Disclaimer
☐ Request for Refund
☐ CD Number of CD(s) _____
  ☐ Landscape Table on CD

☐ After Allowance Communication to TC
☐ Appeal Communication to Board of Appeals and Interferences
☐ Appeal Communication to TC (Appeal Notice, Brief, Reply Brief)
☐ Proprietary Information
☐ Status Letter
☒ Return-Receipt Postcard
☐ Other Enclosure(s) (please identify below):

Remarks

## SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

| Firm or Individual Name | McAndrews Held & Malloy, Ltd. | | |
|---|---|---|---|
| Name (Print/type) | Priscilla Gallagher | Registration No. (Attorney/Agent) | 32,223 |
| Signature | *Priscilla F. Gallagher* | Date: May 10, 2005 | |

## EXPRESS MAIL DEPOSIT

"Express Mail" mailing label number : EV 164037920 US
Date of Deposit May 10, 2005.

PTO/SB/17 (12-04)
Approved for use through 07/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
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# FEE TRANSMITTAL for FY 2005

*Effective on 12/08/2004.*
*Fees pursuant to the consolidated Appropriates Act. 2005 (H.R. 4818).*

☑ Applicant claims small entity status. See 37 CFR 1.27

| Complete If Known | |
|---|---|
| Application Number | 09/981,643 |
| Filing Date | October 16, 2001 |
| First Named Inventor | Leo W.M. Lau, et al. |
| Examiner Name | Archene A. Turner |
| Art Unit | 1775 |

| TOTAL AMOUNT OF PAYMENT | ($) | 750.00 | Attorney Docket No. | CUH-003.00/16678US01 |
|---|---|---|---|---|

## METHOD OF PAYMENT (check all that apply)

☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): _____

☑ Deposit Account  Deposit Account Number: 13-0017     Deposit Account Name: McAndrews Held & Malloy

For the above-identified deposit account, the Director is hereby authorized to (check all that apply)

☑ Charge Fee(s) indicated below          ☐ Charge Fee(s) indicated below, **except for the filing fee**

☑ Charge any additional fee(s) or underpayments of fees(s) ☑ Credit any overpayments
under 37 CFR 1.16 and 1.17

**WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**

## FEE CALCULATION

### 1. BASIC FILING, SEARCH, AND EXAMINATION FEES

| Application Type | FILING FEES Fee ($) | Small Entity Fee($) | SEARCH FEES Fee($) | Small Entity Fee($) | EXAMINATION FEES Fee($) | Small Entity Fee($) | Fees Paid($) |
|---|---|---|---|---|---|---|---|
| Utility | 300 | 150 | 500 | 250 | 200 | 100 | |
| Design | 200 | 100 | 100 | 50 | 130 | 65 | |
| Plant | 200 | 100 | 300 | 150 | 160 | 80 | |
| Reissue | 300 | 150 | 500 | 250 | 600 | 300 | |
| Provisional | 200 | 100 | 0 | 0 | 0 | 0 | |

### 2. EXCESS CLAIM FEES

| Fee Description | | Fee($) | Small Entity Fee($) |
|---|---|---|---|
| Each claim over 20, or for Reissues, each claim over 20 and more than in the original patent | | 50 | 25 |
| Each independent claim over 3 or, for Reissues, each independent claim more than in the original patent | | 200 | 100 |
| Multiple dependent claims | | 360 | 180 |

| Total Claims | | Extra Claims | Fee($) | Fee Paid ($) | Multiple Dependent Claims | |
|---|---|---|---|---|---|---|
| _____ | -20 or HP _____ | x _____ | = _____ | | Fee | Fee Paid ($) |

HP = highest number of total claims paid for, if greater than 20

| Indep. Claims | | Extra Claims | Fee($) | Fee Paid ($) |
|---|---|---|---|---|
| _____ | -3 or HP _____ | x _____ | = _____ | |

HP = highest number of independent claims paid for, if greater than 3

### 3. APPLICATION SIZE FEE

If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

| Total Sheets | | Extra Sheets | | Number of each additional 50 or fraction thereof | Fee($) | Fee Paid($) |
|---|---|---|---|---|---|---|
| _____ | -100 _____ | /50 | _____ (round up to a whole number) | x _____ | = _____ | |

### 4. OTHER FEE(S)

| | Fee Paid($) |
|---|---|
| Non-English Specification, $130 fee (no small entity discount) | _____ |
| Other: Petition under 37 C.F.R. § 1.137(b) | 750.00 |

## SUBMITTED BY

| Signature | *Priscilla F. Gallagher* | Registration No. (Attorney/Agent) | 32,223 | Telephone | (312)775-8000 |
|---|---|---|---|---|---|
| Name (print/type) | **Priscilla Gallagher** | | | Date | May 10, 2005 |

*05/11/05*

*IIw*
*DA* ¢⁢

Attorney Docket No.: CUH-003.00/16678US01

# IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | | |
|---|---|---|
| In the Application of:<br>Leo W.M. Lau, et al. | ) ) ) | **Patent** |
| | ) | <u>CERTIFICATE OF MAILING</u> |
| U.S. Serial No.: 09/981,643 | ) ) | Express Mail No.: EV 164037920 US |
| Filed: October 16, 2001 | ) ) ) | I hereby certify that this correspondence is being deposited with the United States |
| For: DECORATIVE HARD COATING AND METHOD FOR MANUFACTURE | ) ) ) | Postal Service as Express Mail in an envelope addressed to: Mail Stop Petition, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on May 10, |
| Group Art Unit No.: 1775 | ) ) | 2005. |
| Examiner: TURNER, Archene A. | ) ) | By: _Priscilla T. Gallagher_ |
| Confirmation No.: 7018 | ) ) ) | Priscilla Gallagher<br>Reg. No. 32,233 |

## PETITION UNDER 37 C.F.R. § 1.137(b)
## TO REVIVE AN UNINTENTIONALLY ABANDONED
## PATENT APPLICATION

Mail Stop: Petition
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This paper responds to the Notice of Abandonment mailed February 9, 2005 in the above-identified application.

Applicants hereby petition the Commissioner under 37 C.F.R. 1.137(b) to revive the above identified application which was **unintentionally** abandoned based upon a failure to respond to the Office Action mailed July 21, 2004, requesting an election of the claims subject to restriction requirement for examination purpose, for which a response was due August 21, 2004, without an extension of time, and as late as January 21, 2005, with a five (5) month extension of time.

This Petition is accompanied by the following documents:

1.    A Response to the outstanding Office Action mailed July 21, 2004;

2.    A Fee Transmittal authorizing the Commissioner to charge the required amount of $750.00 (small entity) to cover the petition fee under 37 C.F.R. § 1.17(m) to the deposit account of McAndrews, Held & Malloy, Ltd., Account No. 13-0017.

## STATEMENT

The entire delay in filing the required reply from the due date for the required reply until the filing of a grantable petition under 37 CFR 1.137(b) was unintentional.
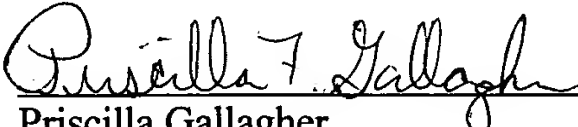
## CONCLUSION

Insofar as all requirements under 37 C.F.R. § 1.137(b) have been met, the entry of the Applicants' petition is respectfully requested.
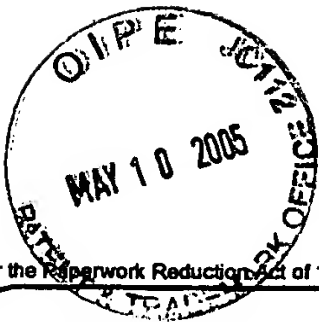
Please charge any additional fees or credit overpayment to the deposit account of McAndrews, Held & Malloy, Ltd., Account No. 13-0017.

Respectfully submitted,

Dated: May 10, 2005          By: _Priscilla J. Gallagher_
                                 Priscilla Gallagher
                                 Reg. No. 32,233
                                 Attorney for Applicants

McANDREWS, HELD & MALLOY, LTD.
500 West Madison Street
Chicago, Illinois 60661
Telephone: (312) 775-8000
Facsimile: (312) 775-8100

| REVOCATION OF POWER OF ATTORNEY WITH NEW POWER OF ATTORNEY AND CHANGE OF CORRESPONDENCE ADDRESS | Application Number | 09/981,643 |
| --- | --- | --- |
| | Filing Date | October 16, 2001 |
| | First Named Inventor | Leo W. M. LAU et al. |
| | Art Unit | 1775 |
| | Examiner Name | Archene A.Turner |
| | Attorney Docket Number | 16678US01 |

I hereby revoke all previous powers of attorney or authorizations of agent given in the above-identified application:

☐ A Power of Attorney is submitted herewith.

*OR*

☒ I hereby appoint the practitioners at Customer Number :   23,446

☒ Please change the correspondence address for the above-identified application to:

☒ The address associated with Customer Number:   23,446

*OR*

| ☒ Firm *or* Individual Name | McAndrews, Held & Malloy, Ltd. | | | | |
| --- | --- | --- | --- | --- | --- |
| Address | 500 W. Madison Street, Suite 3400 | | | | |
| City | Chicago | State | IL | ZIP | 60661 |
| Country | USA | | | | |
| Telephone | (312) 775-8000 | Fax | (312) 775-8100 | | |

I am the:

☐ Applicant/Inventor.

☒ Assignee of record of the entire interest.  See 37 CFR 3.71.
*Statement under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96)*

### SIGNATURE of Applicant or Assignee of Record

| Signature | |
| --- | --- |
| Name | Ms. NGAN Alice Man Wai |
| Date | 06 MAY 2005 | Telephone | 312-775-8000 |

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below*.

☒    *Total of 1 forms are submitted.

*If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.*

## STATEMENT UNDER 37 CFR 3.73(b)

Applicant/Patent Owner: Leo W.M. LAU et al.

Application No./Patent No.: 09/981,643      Filed/Issue Date: October 16, 2001

Entitled: Decorative hard Coating and Method for Manufacture

The Chinese University of Hong Kong    , a  university 

          (Name of Assignee)                       (Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that it is:

1. ☒   the assignee of the entire right, title, and interest; or

2. ☐   an assignee of less than the entire right, title, and interest

        The extent (by percentage) of its ownership interest is _____ %

in the patent application/patent identified above by virtue of either:

A. ☒ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel 012927, Frame 0879, or for which a copy thereof is attached.

OR

B. ☐ A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as shown below:

     1. From:_____            To:_____
        The document was recorded in the United States Patent and Trademark Office at
        Reel _____, Frame _____, or for which a copy thereof is attached.

     2. From:_____            To:_____
        The document was recorded in the United States Patent and Trademark Office at
        Reel _____, Frame _____, or for which a copy thereof is attached.

     3. From:_____            To:_____
        The document was recorded in the United States Patent and Trademark Office at
        Reel _____, Frame _____, or for which a copy thereof is attached.

     ☐ Additional documents in the chain of title are listed on a supplemental sheet.

☐ Copies of assignments or other documents in the chain of title are attached.

[NOTE: A separate copy (i.e., a true copy of the original document(s)) must be submitted to Assignment Division in accordance with 37 CFR Part 3, if the assignment is to be recorded in the records of the USPTO. See MPEP 302.08]

The undersigned (whose title is supplied below) is authorized to act on behalf of the assignee.

| | |
|---|---|
| _(signature)_ | May 6, 2005 |
| Signature | Date |
| Ms. NGAN, Alice Man Wai | 852-2609-8884 |
| Printed or Typed Name | Telephone Number |
| Director, Research and Technology Administration Office | |
| Title | |

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In the Application of:<br>Leo W.M. Lau, et al. | )<br>)<br>)<br>) |
| U.S. Serial No.: 09/981,643 | )<br>) |
| Filed: October 16, 2001 | )<br>)<br>) |
| For: DECORATIVE HARD COATING<br>AND METHOD FOR MANUFACTURE | )<br>)<br>)<br>) |
| Group Art Unit No.: 1775 | )<br>)<br>) |
| Examiner: TURNER, Archene A. | )<br>)<br>) |
| Confirmation No.: 7018 | )<br>)<br>)<br>) |

**Patent**

**CERTIFICATE OF MAILING**

**Express Mail No.: EV 164037920 US**

I hereby certify that this correspondence is being deposited with the United States Postal Service as Express Mail in an envelope addressed to: Mail Stop Petition, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on May 10, 2005.

By: _Priscilla F. Gallagher_
Priscilla Gallagher
Reg. No. 32,223

## AMENDMENT

Mail Stop Petition
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

This paper responds to the Office Action in the above-entitled application, mailed July 21, 2004, requesting an election of the claims subject to restriction requirement for examination purpose, for which a response was due August 21, 2004, without an extension of time, and as late as January 21, 2005, with a five (5) month extension of time. This paper is being filed accompanying a Petition Under 37 C.F.R. 1.137(b) To Revive An Unintentionally Abandoned Patent Application.

Please amend the above-identified application as follows.

- **Election Of Claims And Species** begins on page 2 of this paper.

- **Amendments to the Claims** are reflected in the listing of claims, which begins on page 3 of this paper.

- **Remarks** begin on page 10 of this paper.

## Election Of Claims And Species

The Applicant hereby elects Group I, claims 1-8, 10, 12-14, 52-53 with traverse.

## Amendments To The Claims

A complete list of all the presently or formerly pending claims in the application is provided below, with suitable headings to show the status of each claim and, where appropriate, its current text. This listing of claims will replace all prior versions, and listings of claims in this application.

**Listing of Claims:**

1-5.     (Cancelled).

6.      (Previously presented) A decorative hard coating composition comprising zirconium-aluminium oxycarbonitride, having a lower atomic concentration of aluminium than of zirconium.

7.      (Previously presented) A decorative hard coating composition comprising zirconium-aluminium oxycarbonitride, wherein atomic concentration of aluminium is less than about one fifth that of zirconium.

8.      (Previously presented) A decorative hard coating composition comprising zirconium-aluminium oxycarbonitride, having relative atomic concentrations of Zr:Al:N:O:C of approximately 56:10:23:7:4.

9.      (Previously presented) A decorative hard coating comprising metal-rich zirconium-aluminium oxycarbonitride, overlying a substrate, wherein the decorative hard coating further comprises an intermediate layer of a metal, alloy or metal-rich metal oxycarbonitride.

10.     (Cancelled)

11.     (Previously presented) A decorative hard coating comprising metal-rich zirconium-aluminium oxycarbonitride, overlying a substrate of metal, plastic, or ceramic.

12-13. (Cancelled).

14.     (Currently amended) The decorative hard coating composition as in ~~claim 13~~ claim 6, ~~wherein the decorative hard coating consists substantially~~ consisting essentially of zirconium-aluminium oxycarbonitride.

15.     (Cancelled).

16.     (Previously presented)   A coated article comprising a substrate and a decorative hard coating above the substrate that comprises metal-rich oxycarbonitrides of zirconium and aluminium.

17.     (Cancelled).

18.     (Previously presented)   A decorative hard coating comprising an aluminium or metal-rich aluminium oxycarbonitride layer on a metal-rich zirconium oxycarbonitride layer.

19.     (Original)   The decorative hard coating as in claim 18, wherein the zirconium-rich oxycarbonitride layer has a CIELAB '|b|' value of greater than about five, and the overall decorative hard coating has a CIELAB '|b|' value of at most about five.

20.     (Original)   The decorative hard coating as in claim 18, having a CIELAB color of 'L' of at least about 76, '|a|' of at most about 1, and '|b|' of at most about five.

21.     (Original)   The decorative hard coating as in claim 18, having a Vickers hardness of at least about 15 GPa.

22.     (Previously presented)   A decorative hard coating comprising an overlayer comprising aluminium or metal-rich aluminium oxycarbonitride or aluminium-zirconium oxycarbonitride, the overlayer overlying a metal-rich metal oxycarbonitride layer, the decorative hard coating:

4

having a CIELAB color of 'L' of at least about 76, '|a|' of at most about 1, and '|b|' of at most about five; or

having a Vickers hardness of at least about 15 GPa.

23.    (Previously presented)   A decorative hard coating comprising an overlayer comprising aluminium or metal-rich aluminium oxycarbonitride or aluminium-zirconium oxycarbonitride, the overlayer overlying a metal-rich metal oxycarbonitride layer, the decorative hard coating having a CIELAB color of 'L' of at least about 76, '|a|' of at most about 1, and '|b|' of at most about five.

24.    (Previously presented)   A decorative hard coating comprising an overlayer comprising aluminium or metal-rich aluminium oxycarbonitride or aluminium-zirconium oxycarbonitride, the overlayer overlying a metal-rich metal oxycarbonitride layer, the decorative hard coating having a Vickers hardness of at least about 15 GPa.

25.    (Original)   The decorative hard coating as in claim 22, applied to a substrate and further comprising a layer of metal, alloy, or metal oxycarbonitride.

26.    (Original)   A decorative hard coating comprising an underlayer and an overlayer, wherein the underlayer comprises metal-rich oxycarbonitride, and the overlayer comprises aluminium in some form.

27.    (Original)   The decorative hard coating as in claim 26, wherein the underlayer has a CIELAB color value '|b|' of greater than about five, and the decorative hard coating has a CIELAB color value '|b|' of at most about five.

28.    (Original)   The decorative hard coating as in claim 26, wherein the overlayer comprises aluminium in the form of aluminium oxycarbonitride or metallic aluminium.

29.    (Previously presented)   The decorative hard coating as in claim 26, wherein the metal-rich oxycarbonitride comprises zirconium oxycarbonitride.

5

30.    (Previously presented)   The decorative hard coating as in claim 26, wherein the metal-rich oxycarbonitride comprises zirconium oxycarbonitride or stainless steel.

31.    (Previously presented)   The decorative hard coating as in claim 26, wherein the overlayer consists substantially of aluminium or metal-rich aluminium oxycarbonitride, and the underlayer consists substantially of metal-rich oxycarbonitride.

32.    (Original)   The decorative hard coating as in claim 26, having thickness of about 0.2 micron to about 3 microns.

33.    (Original)   The decorative hard coating as in claim 26, wherein the underlayer has a CIELAB '|b|' value of greater than about five, and the decorative hard coating has a CIELAB '|b|' value of at most about five.

34.    (Original)   The decorative hard coating as in claim 26, having a CIELAB color of 'L' of at least about 76, '|a|' of at most about 1, and '|b|' of at most about five.

35.    (Original)   The decorative hard coating as in claim 26, having a Vickers hardness of at least about 15 GPa.

36.    (Original)   The decorative hard coating as in claim 26, having a Vickers hardness of at least about 15 GPa and a CIELAB color of 'L' of at least about 76, '|a|' of at most about 1, and '|b|' of at most about five; wherein the underlayer has a CIELAB 'b' value of greater than about five.

37.    (Original)   The decorative hard coating as in claim 26, deposited on a substrate by evaporation, arc deposition, sputtering, or a combination thereof.

38.    (Previously presented)   A method of making a metallic white decorative coating comprising:

6

providing a substrate; and

forming a layer of zirconium-aluminium oxycarbonitride over the substrate, the layer having a lower atomic concentration of aluminium than of zirconium.

39.     (Original)   The method according to claim 38, wherein the forming step comprises arc depositing zirconium and magentron sputtering of aluminium, with a gas mixture of argon, nitrogen, oxygen, and acetylene.

40.     (Previously presented)   A method of making a metallic white decorative coating comprising:

providing a substrate;

forming an underlayer, comprising metal-rich oxycarbonitride, over the substrate; and

forming an overlayer, comprising aluminium or metal-rich aluminium oxycarbonitride over the underlayer.

41.     (Previously presented)   The method according to claim 40, wherein the step of forming the underlayer comprises depositing zirconium and aluminium, with a gas mixture including at least nitrogen.

42.     (Previously presented)   The method according to claim 40, wherein the metallic white coating has a CIELAB color of 'L' of at least about 76, '|a|' of at most about one, and '|b|' of at most about five.

43.     (Previously presented)   A method of producing an article that is coated according to the method according to claim 40, the producing method comprising the providing step and the forming steps, wherein the providing step comprises providing, as the substrate, an article to be coated.

44.     (Previously presented)   A coated article produced according to the producing method according to claim 43.

7

45.    (Previously presented)   A method of forming a decorative coating on a substrate, the method comprising:

forming a metal-rich layer over the substrate, the metal-rich layer comprising zirconium-aluminium oxycarbonitride.

46.    (Previously presented)   The method according to claim 45, wherein the forming step comprises forming the metal-rich layer using physical vapor deposition.

47.    (Previously presented)   The method according to claim 45, wherein the layer has a CIELAB color of 'L' of at least about 76, '|a|' of at most about one, and '|b|' of at most about four.

48.    (Previously presented)   A method of producing an article that is coated according to the method according to claim 45, the producing method comprising:

providing, as the substrate, an article to be coated; and

the forming step.

49.    (Previously presented)   A coated article produced according to the producing method according to claim 48.

50.    (Previously presented)   A method of forming a decorative coating on a substrate, the method comprising:

forming a layer comprising zirconium-aluminium oxycarbonitride having a CIELAB color of 'L' of at least about 76, '|a|' of at most about one, and '|b|' of at most about five.

51-52. (Cancelled) .

53.    (Currently amended)   A̶ The decorative hard coating composition according to claim 6, wherein the zirconium-aluminium oxycarbonitride comprises metal-rich zirconium-aluminium oxycarbonitride.

8

54.     (Previously presented)   An article coated with the decorative hard coating composition according to claim 6.


55.     (Cancelled).


56.     (Previously presented)   A method of making a metallic white decorative coating comprising:

providing a substrate; and

forming a layer of zirconium-aluminium oxycarbonitride over the substrate, the layer having a lower atomic concentration of aluminium than of zirconium;

wherein the forming step comprises employing physical vapor deposition.


57.     (Previously presented)   A method of making a metallic white decorative coating comprising:

providing a substrate; and

forming a layer of zirconium-aluminium oxycarbonitride over the substrate, the layer having a lower atomic concentration of aluminium than of zirconium;

wherein the layer has a CIELAB color of 'L' of at least about 76, '|a|' of at most about one, and '|b|' of at most about five.


58.     (Previously presented)   An article coated according to a method of making a metallic white decorative coating, the method comprising:

providing a substrate; and

forming a layer of zirconium-aluminium oxycarbonitride over the substrate, the layer having a lower atomic concentration of aluminium than of zirconium.


59-62. (Cancelled).

## Remarks

### Restriction Requirement

The present Office Action holds that the inventions represented by Group I (claims 1-8, 10, 12-14, 52-53), Group II (claims 9, 11, 16, 18-37, 44, 49, 54, 58-62), Group III (claims 15, 17, 51, 55) and Group IV (claims 38-43, 45-48, 50, 56-57) are distinct, each from the other, and therefore are subject to restriction and/or election requirement. An election of Group I for examination has been made with traverse.

The restriction requirement is respectfully traversed because, "[i]f the search and examination of an entire application can be made without serious burden, the examiner must examine it on the merits, even though it includes claims to distinct or independent inventions." Manual of Patent Examination Procedure ("MPEP"), § 803, page 800-4 (8th Ed. Rev. 2, 2004). One of the "two criteria for a proper requirement for restriction between patentably distinct inventions" is that "[t]here must be a serious burden on the examiner if restriction is not required ...." MPEP § 803, page 800-4 (emphasis added). The fields of search required to search the respective composition of Group I, coating of Group II, article of Group III and the method of Group IV are essentially coextensive, because they are all defined, directly or indirectly, by a decorative hard coating composition comprising a metal oxycarbonitride (e.g., zirconium, aluminum, or zirconium-aluminum oxycarbonitride). Therefore, there will be no extra burden on the Examiner to examine all claims.

More importantly, the Office has already conducted search(es) and substantive examination of all groups of claims in the present application, as evidenced by the two Office Actions mailed March 14 and December 2, 2003. In fact, in these two Office Actions, the previous Examiner indicated that various claims (6-8, 38, 39, 50, and 56-58) from Groups I, II and IV, as categorized by the present Examiner, were either allowed or allowable if rewritten into independent form. Therefore, Applicants believe that there would be no serious burden on the present Examiner to examine all four groups of clams based on the search(es) and examination already done by the previous Examiner. And therefore, Applicants respectfully submit that the restriction and/or election requirement should be withdrawn.

### Claims of the Elected Group I (1-8, 10, 12-14, 52-53)

In order to expedite the examination process, claims 1-5, 9-13, and 52 of the elected Group I have been cancelled and claim 14 of the elected Group I has been amended to depend from claim 6.

10

Applicants respectfully submit that all pending claims of Group I (6-8, 14 and 53) are allowable for the reasons stated below.

In the Office Action mailed March 14, 2003, the Examiner indicated that claims 6-8 "would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims." In the Response mailed September 15, 2004, to that Office Action, Applicants amended claims 6-8 in the manner as suggested by the Examiner.

In the Office Action mailed December 2, 2003, which was made final by the Examiner, claims 6-8 were rejected, among other claims, under 35 U.S.C. § 112, second paragraph, as being indefinite. The Examiner suggested Applicants to use the preamble reciting "A decorative hard composition comprising..." for these claims. In the Response filed June 2, 2004, accompanying the Request for Continued Reexamination (RCE), claims 6-8 were amended in the manner suggested by the Examiner.

In this paper, the previously presented claims 6-8 are kept unchanged as three independent claims, and therefore, should be allowable as indicated by the Office Actions of March 14 and December 2, 2003.

Claim 14 has been amended to depend from claim 6. Therefore, it should be allowable at least for the same reasons as those for claim 6.

Claim 53 also depends from claim 6. In the Office Action mailed December 2, 2003, claim 53 was rejected under 35 U.S.C. § 112, second paragraph, as being rendered indefinite by the use of the term "metal-rich." Applicants have fully addressed this rejection in the Response filed June 2, 2004:

> Applicants respectively point out Metal-rich is a well known adjective used by chemists and materials scientists to describe a compound having more metal than what would be considered to be within its normal stoichiometric composition. For example, $ZrO_2$ and $ZrN$ are the stoichiometric compositions for Zirconium oxide and nitride. Thus an example compound having a Zr/O ratio that is an amount higher than one-half is an example of metal-rich zirconium oxide, and an example compound having a Zr/N ratio that is an amount higher than 1 is an example of metal-rich zirconium nitride.

To further show that the term "metal-rich" recited in claim 53 is an established term known to a person of ordinary skill in the art when the present application was filed, a 2001 journal article is attached to this paper as Exhibit A. In this article, its authors studied and compared metal-rich oxide samples to stoichiometric oxides. See, Exhibit A, page i152. It is believed that Applicants have

clarified the meaning of the term "metal-rich" recited in the present application and overcome the indefiniteness rejection of claim 53. It is therefore respectfully submitted that claim 53 is definite under 35 U.S.C. § 112, second paragraph, and is allowable.

**Claims of Groups II-IV**

All claims of Group III (15, 17, 51 and 55) have been cancelled. Therefore, the restriction requirement regarding Group III is moot.

To further expedite the examination process, claims 59-62 of Group II have been cancelled.

Claims 38, 39 and 50 of Group IV have been allowed by the Office Action mailed December 2, 2003. The same Office Action objected claims 56-58 as being dependent on rejected base claim, but indicated that they would be allowable if rewritten in independent form. Claims 56-58 have been rewritten into independent claims by the Response filed June 2, 2004, and therefore are now allowable.

The rejections to other pending claims of nonelected Groups II and IV (9, 11, 16, 18-37, 40-49 and 54) have been fully addressed in the Response filed June 2, 2004. Applicants would not repeat them here.

No new matter has been introduced by the amendments made in this paper. Applicants respectfully submit that all pending claims of elected Group I (6-8, 14 and 53) and nonelected Groups II and IV (9, 11, 16, 18-50, 54, and 56-58) have met all requirements of the patent law, and therefore are patentable.
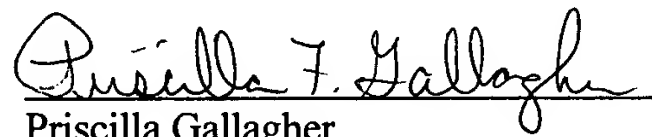
## Conclusion

In view of the above remarks, Applicants respectfully requests reconsideration of the present application, and allowance of all pending claims (6-9, 11, 14, 16, 18-50, 53, 54, and 56-58); or, as an alternative if the Examiner refuses to withdraw the restriction requirement, allowance of all pending claims of the elected Group I (6-8, 14 and 53).

The Commissioner is hereby authorized to charge any additional fees or credit any overpayment, to Deposit Account No. 13-0017.

Respectfully submitted,

DATE:  May 10, 2005

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13

# Study of Bimetallic Interactions Between Transition- and s,p-Metals: Pd/AlO$_x$ and Pd/SnO$_x$ Catalysts and Sensors

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The metal-substrate and metal-metal interactions (MSI, MMI) represent important effects determining the properties of supported catalysts and gas sensors. We investigate the MSI and MMI effects by X-ray Photoelectron Spectroscopy (XPS), Low Energy Ion Scattering (LEIS) and Thermal Desorption Spectroscopy (TDS) in the case of Pd films vapor deposited on more or less stoichiometric aluminum and tin oxide substrates and on pure Pd and Sn, respectively. The observed MSI is explained by the formation of an intermetallic interface exhibiting a strong bimetallic Pd/Al(Sn) interaction. In the case of more metal rich substrates the Pd - Al(Sn) surface alloy layers exhibit noble metal-like valence-band structure and low CO desorption temperature. The fundamental studies of Pd/Al(Sn) bimetallic alloys are of importance due to the role that they play in modification of chemisorption, catalytic and sensing properties of real Pd/Al(Sn)-oxide systems as well as in the realization of novel Pd-alloy catalysts.

Modern catalysts and gas sensors are generally composed of several elements in precise proportions. They are optimised in order to give the highest reaction rate and to have the best selectivity. The optimisation is mainly based on empirical approaches and often it is not possible to describe the details of the reaction mechanisms taking place during catalytic reaction. This is partially due to the complexity of these systems, and also to the lack of their characterization.

For this reason the adsorption and reaction studies are often performed on well-defined model systems, i.e., on single crystals and supported ultra-thin metallic layers, under in situ low pressure reaction conditions. Model catalysts and sensors can be fully characterised by the numerous surface-science techniques available.

The CO adsorption on Pd-alumina model catalysts has been studied extensively in the past by means of different surface sensitive techniques, as can be seen in references.[1-16] Numerous studies have been devoted namely to the investigation of so-called size effect - size and morphology dependent properties. The results have often been rather contradictory, showing the complexity of the problem.

Semiconductor gas sensors based on tin dioxide are widely used for the detection of toxic and explosive gases in air. The general operation mechanism of gas detection by a change in surface conductivity has been widely described in the literature.[17-21] In an atmosphere of air containing inflammable gases gas molecules react with the surface-adsorbed $O^{2-}$ and release electrons. The bonding of transition metal atoms (Pd, Pt, Ag) at surface or bulk sites influences considerably the sensor response. Two possible sensitization mechanisms have been proposed[22] an electronic effect (direct exchange of electrons between the semiconductors and the metal additive particles) and a catalytic one (metallic clusters activate the gaseous species).

Studies of Pd interaction with Al and Sn showed very similar evolution of the Pd $d$-band. At room temperature, Pd intermixed with the substrate forming a thin surface alloy. Photoemission results showed a strong interaction between Pd and Al (Sn), through the hybridisation of the Pd $d$ and Al (Sn) $s$-states, leading to the formation of alloy of noble metal-like electronic structure with the $d$-band centred at 4 eV below Fermi level.[23, 24]

The CO adsorption-desorption studies on Pd/Al systems[25] showed an important decrease of the CO desorption temperature, accompanied by a partial CO dissociation and formation of Al-related oxidic and carbidic species.

In this work the Pd-Al and Pd-Sn bimetallic interactions are considered as a possible effect determining palladium-substrate interaction, which influences properties of Pd/AlOx and Pd/SnO$_x$ systems. Especially in the case of reduced (metal rich) oxide substrate surfaces, this interaction can play important role via surface morphological changing and/or via alterations of Pd catalytic properties. A striking similarity between properties of both, aluminum and tin oxide, systems is shown.

## Experimental

In these studies we used the methods of Thermal Desorption Spectroscopy (TDS), X-ray Photoelectron Spectroscopy (XPS) and Low Energy Ion Scattering (LEIS). The experiments have been carried out in two ultra-high vacuum (UHV) chambers. For TDS studies, the UHV system was equipped with a specially designed desorption spectrometer, described in.[25] CO exposure was provided by a molecular beam doser direct to the surface, so that relatively high exposures of the sample were possible, while a low pressure in the chamber was maintained. A linear heating rate was achieved with a thermoelectric programmer.

XPS and LEIS experiments were performed in the second chamber using the OMICRON EA 125 multichannel hemispherical analyzer, a dual Al/Mg X-ray source and a differentially pumped ion gun. The substrates were cleaned by Ar$^+$ ion bombardment.

Two aluminum oxide substrates with different surface stoichiometry were used as a model support. Stoichiometric singlecrystalline α-alumina (0001) and aluminum rich AlO$_x$ film,

prepared by $Ar^+$ ion bombardment of a native oxide film on chemically cleaned polycrystalline Al foil (99.999% purity). The cleanliness of the surface as well as the effect of preferential sputtering of oxide surface compounds was monitored by means of XPS and LEIS analysis during the bombardment. LEIS was carried out using $He^+$ ions at primary energy 2 keV.

Similarly two tin oxide substrates, with various surface stoichiometry, were used as a support. $SnO_2$ thin polycrystalline samples with thickness of 30-70 nm were deposited by spray pyrolysis method, using 0.2M $SnCl_4$-water solution ($T_{pyr}$ = 350° C).[26] Films were deposited on low resistivity Si (111) substrates to minimize charging effect during XPS measurements. The more stoichiometric (110) surface was prepared by cutting a natural $SnO_2$ crystal (cassiterite). The substrates were heated in vacuum ($10^{-7}$ Pa, 500 K, 10 min) and cleaned by argon ion bombardment (500 eV) in order to remove the residual surface contamination.

The palladium was deposited on the aluminum oxides in situ at room temperature using the micro electron beam evaporation source permitting to control the evaporation rate by monitoring the $Pd^+$ ion current. We used a constant deposition rate of $1.5\times10^{12}$ atoms $s^{-1}$, the value of which was determined from the XPS data.

## Results and discussion

Pd was deposited step-likely on Al and Sn oxide substrates as well as on reference metallic Al and Sn. The film growth was investigated by combining XPS and LEIS method. Bulk $\alpha$-alumina and cassiterite exhibited nearly stoichiometric surfaces, whilst the XPS and LEIS quantitative analysis indicated non-stoichiometric oxide surfaces in the case of both oxide films substrates. The intensity ratio of core level metal and oxygen XPS peak gave $AlO_x$ and $SnO_x$ stoichiometry with x near unity. $He^+$ ion scattering spectra, which provided the information on the first layer composition, showed only a small residual oxygen signal, O/Al and O/Sn intensity ratio being 0.13 and 0.042, respectively. The most probable explanation of this discrepancy was the presence of a metal-rich thin surface layer, which influenced the "average" value of the metal (Al, Sn) concentration, obtained by the quantitative analysis over the thicker surface region, given by the XPS information depth.
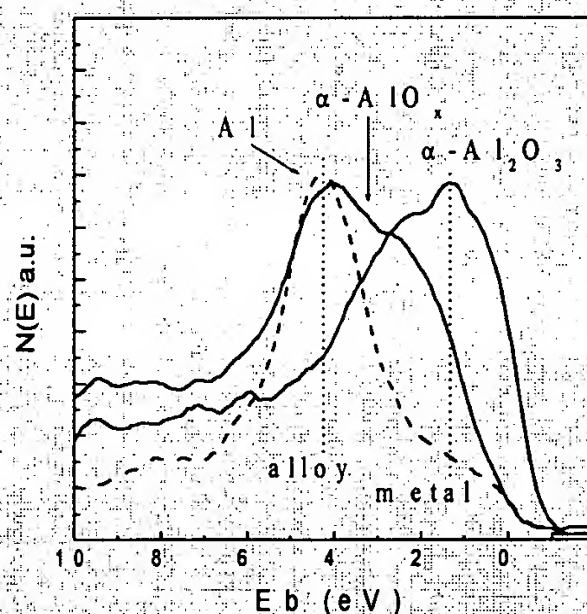


Fig. 1 Valence band spectra of Pd deposited on $Al_2O_3$, $AlO_x$ and Al substrates.

In Fig. 1 and 2 we compared the valence band spectra obtained with Mg K$\alpha$ excitation for all the substrates mentioned above, after depositing of equivalent of 2 ML of palladium. The observed effect of Pd-Al and Pd-Sn interaction was the spectacular shift of the Pd 4d-centroid to higher binding energy. The PdAl and PdSn bulk alloy, formed on pure metallic substrates, exhibited the single maximum at 4.3 eV and 4.0 eV, respectively. 4d band of Pd/metal-rich oxide samples consisted of "metallic" and "alloy" contributions, whilst Pd on stoichiometric oxides had the valence band typical for Pd metal.
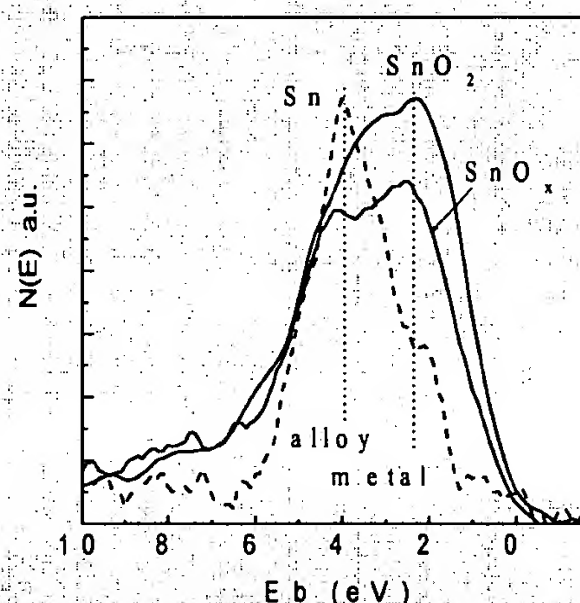


Fig. 2 Valence band spectra of Pd deposited on $SnO_2$, $SnO_x$ and Sn substrates.

Comparing Fig. 1 and 2 we can see very similar behavior. Pd forms alloy interface on pure metal and metal-rich substrates with the similar d-centroid shift effect caused by the transition-metal/s,p-metal bimetallic interaction, induced by a strong hybridisation of the Pd-d and Al-s,p and Sn-s,p states.

LEIS investigation of relative oxygen/metal concentration showed rather interesting effect of oxygen surface coverage increase with increasing amount of deposited Pd. The results are presented in Tab. 1. For clarity the values are normalized to unity, i.e., relative coverages are taken unity for both bare substrates. The corresponding non-normalized oxygen surface concentration values are indicated in brackets.

Table 1 Relative surface oxygen concentration for different amounts of deposited Pd

| Pd amount [ML] | Relative variations of surface oxygen coverage | |
| --- | --- | --- |
| | Sample: Pd/AlO$_x$ | Sample: Pd/SnO$_x$ |
| 0 | 1(0.13) | 1(0.042) |
| 1 | 1.27 | 1.29 |
| 2 | 1.37 | 1.62- |
| 4 | 1.07 | 2.22 |

It can be seen that oxygen/metal ratio increases with the increasing amount of deposited Pd (it should be noted that the ratio is calculated by dividing the oxygen signal by the sum of Pd and Al (or Sn) intensities, taking the difference in sensitivity factors for O and metals into account). This behaviour can be explained by the effect of PdAl and PdSn intermetallic compound formation, that is characterised by a high cohesion energy. The high surface free energy of the alloy leads to the formation of island structure (which is in agreement with the results of XPS inelastic background shape analysis – not shown) and to the partial discovering of a bare oxide surface (non covered by a continuous metal-rich overlayer).[24, 28] On $AlO_x$

substrate the maximum value is reached for 2 ML of deposited Pd and then it decreases, probably due to the formation of Pd particles on the surface, which is typical for Pd/aluminum oxide systems. It can be well seen in Fig. 3, where the variations of Al, Pd and oxygen concentration are plotted in details. Aluminum surface atoms are progressively replaced by palladium ones showing well that during the first stage of growth Pd is bonded to Al atoms and not to oxygen sites
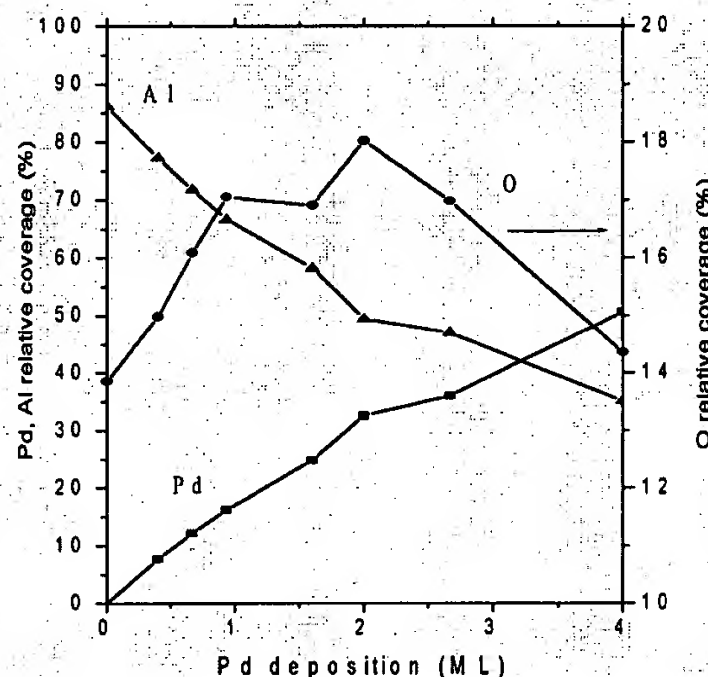


Fig. 3 Aluminum, palladium and oxygen relative coverage variations verus amount of Pd deposited on $AlO_x$ substrate.

On tin oxide this behavior is more pronounced showing higher content of surface oxygen. This effect should influence the surface conductivity considerably which could be taken into account in models explaining a strong variations of tin oxide based sensors characteristics with addition of Pd.

Pd – s,p- metal alloying leads to the important decrease of CO desorption temperature, which can be explained using the molecular-orbital model[29], involving a $5\sigma$ CO donation to the metal associate orbitals, with a back-donation to the empty $2\pi*$ CO orbitals. The subtle balance between the filling of these orbitals, as well as the population of $2\pi*$ CO antibonding level (that weaken, i.e., activate, C-O bond), influences the strength of the metal-CO bond. Pd has the electronic configuration $4d^{9.5}5s^{0.5}$ in the bulk, that is characterised by a narrow high-lying d-band, which allows an important back-donation to $2\pi*$ CO orbital, favoring adsorption on the highly co-ordinate sites with high binding energy. If the centre of Pd d-band is pushed toward higher binding energies, due to the formation of a bimetallic bond, i.e., away from the $2\pi*$ CO orbitals, Pd $4d$- CO $2\pi*$ bonding interactions are weaker[30].

The same behavior is observed in the case of Pd-Al and Pd-Sn interfacial alloy layer formation on non-stoichiometric surfaces of aluminum oxide and tin oxide substrates. In Fig. 4 we compare three CO TDS features obtained for the CO saturation exposure on the reference bulk Pd(111) crystal[8], and on 1 ML of Pd deposited on $AlO_x$ and $SnO_x$ substrates (this work). Considerable shift to lower desorption temperatures can be seen.

This behavior can be explained in the full agreement with XPS valence band structure observation, presented in Fig. 1 and 2, by important Pd-Al and Pd-Sn bimetallic interactions for both non stoichiometric substrates. 1 ML of deposited Pd leads to the formation of surface alloy phases, as concluded also from LEIS results presented in Tab. 1, which are characterized by

appearance of low temperature CO desorption features between 350 and 400 K for PdAl and PdSn, respectively.
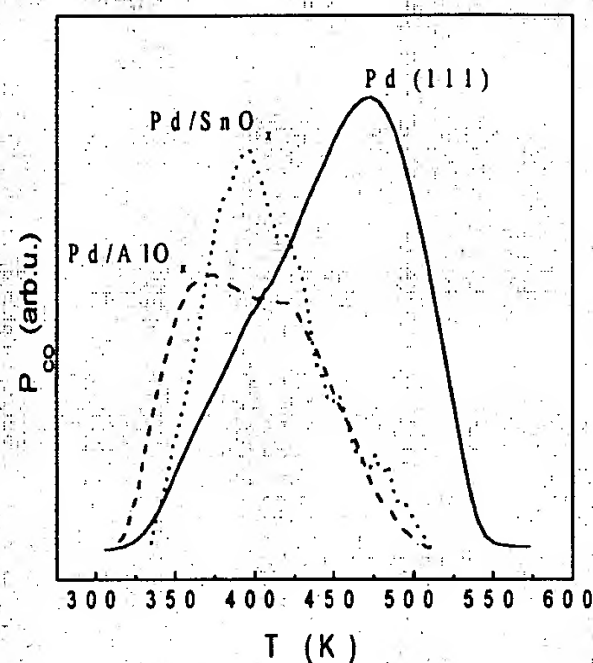


Fig. 4 CO desorption spectra from different Pd samples corespondind to the saturation CO exposure of 10 L ($1\times10^{-5}$ torr s).

These results allows us to conclude that Pd-Al interactions should be considered as an alternative way how to explain the size dependent CO desorption properties of small palladium particles deposited on alumina[8]. It permits us to explain in a very straight way the appearance of low temperature CO desorption features and a general decrease of CO desorption temperature with decreasing Pd particle size on alumina. It is evident that smaller particles should be more influenced by small amount of metallic interfacial aluminum.

## Conclusion

The XPS/LEIS combined study of $AlO_x$ and $SnO_x$ thin film with oxygen deficient surface shows the formation of Al and Sn rich adlayer having metallic character. Small amount of deposited Pd leads to the formation of non-continous film having Pd-Al(Sn) bimetallic character. Substrate metal atoms are bonded to Pd ones due to the strong intermixing, typical for transition-/s,p- metal interaction. The rearrangement of the surface structure leads to the appearance of the oxygen sites at the surface.

CO desorption experiments show the weak CO bonds for low deposited Pd quantity. This is a typical behaviour of CO adsorption on Pd/s,p- alloys that confirms the presence of the bimetallic phase on the investigated surfaces. The weakening of the CO bond strength for the bimetallic phase could be one of origins of the lowering of tin oxide sensors' working temperature by doping them by palladium.

Lowering of CO desorption temperature with decreasing size of Pd-alumina supported particles, which is inconsistent with the general prediction of higher adsorption energy on low coordinated sites, is explained by a possible formation of a Pd-Al intermetallic interface and formation of bimetallic-like adsorption sites. These results should be taken into account in explaining not only the different CO bonding on Pd model catalysts, but also in explaining the different "reactive properties" of technological alumina powders used as supports in heterogeneous catalysis.

The comparative results show in a straight way very similar properties of both, aluminum and tin oxide substrates where the excess of the surface metallic phase conduce to the formation of

an interfacial bimetallic layer with palladium exhibiting very similar electrochemical properties.

## Acknowledgement

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